Some Novel Reactions of Perfluoro-2,3-dialkyloxaziridines

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Perfluoro-2,3-dialkyloxaziridines rearrange at 120–160 °C into $R_fN=CF-OR'_f$ quantitatively. Reaction with SbF_5 at elevated temperature leads to the formation of the isomeric alkoxy imines $R_fON=CFR'_f$. Reaction with CsF in the absence of a solvent results in formation of a mixture of the corresponding acyl fluoride $R'_fC(O)F$ and N-fluoro imine $R'_fCF=NF$. In contrast, reaction between perfluoro-2-butyl-3-propyloxaziridine and CsF in MeCN produces $C_4F_9ON=CFC_3F_7$. Interaction of this oxaziridine with polyfluoro ketones and COF_2 in the presence of CsF in polar solvents leads to the formation of alkoxy imines $R''_fON=CFC_3F_7$.

The chemistry of perfluorooxaziridines is represented mainly by the reactions of perfluoro-2-azapropene oxide (PFAPO) and it includes interaction of PFAPO with nucleophiles,[1] SbF_5,[2] and cycloadditions with alkenes and ketones.[3] Related reactions have also been demonstrated with 2-perhalogeno-alkyl-3,3-difluorooxaziridines.[4] Among the known reactions of other oxaziridines are the interaction of the oxide of the dimer of perfluoro-2-azapropene with caesium fluoride,[5] the thermal rearrangement of 2,3,3-tris(trifluoromethyl)oxaziridine[6] and oxygen-transfer reactions of PFAPO and 2,3,3-tris(trifluoromethyl)oxaziridine with alkenes,[3-6] dimethyl sulfide and pyridine.[6] Recently a new and efficient route for the preparation of perfluoro-2,3-dialkyloxaziridines was discovered, making these compounds readily available for the first time.[7] Investigation of the chemical properties of these compounds demonstrated that they are quite different from previously known oxaziridines. In particular, the new oxaziridines undergo novel rearrangements to form ethers of the type $R_fON=CFR'_f$ and $R_fN=CFOR'_f$ and are much less susceptible to ring opening by nucleophiles.

Results and Discussion

Thermal rearrangement.—Perfluoro-2,3-dialkyloxaziridines 1–3 are stable at room temperature and can be stored at 22 °C indefinitely. At elevated temperatures, compounds 1–3 rearrange to the vinyl ethers 4–6 in quantitative yield.

This unusual rearrangement is assumed to occur by a ring opening *via* the nitrogen–oxygen bond to give a diradical species $R_f\dot{N}-C(-O^•)FR'_f$. Based on $CF_3\overline{N-C(CF_3)_2O}$, which undergoes thermal rearrangement to $(CF_3)_2NC(O)CF_3$,[6] one might have expected $R_fR'_fNC(O)F$ to be the product in this case. Instead, R'_f migrates to the oxygen atom, followed by formation of the carbon–nitrogen double bond. The simple 2 + 3 cycloaddition reaction of PFAPO with fluorinated alkenes[3] is not found for $CF_3\overline{N-C(CF_3)_2O}$,[6] or for substrates 4–6.[8] This difference may be due to the inherent stability of $CF_3\dot{N}CF_2O^•$ where the breaking of a carbon–fluorine bond would be required for a rearrangement similar to that of $CF_3\overline{N-C(CF_3)_2O}$ or compounds 4–6.
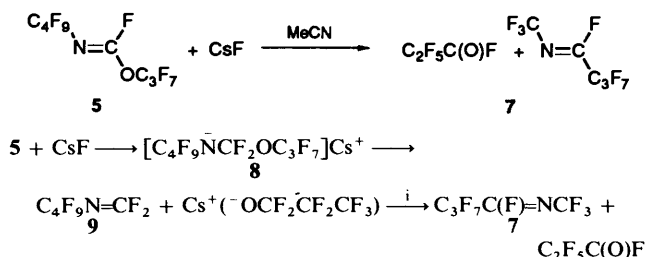
Ethers 4–6 are colourless liquids with good solubility in organic solvents. The IR spectra exhibit a characteristic strong absorption near 1770 cm^{-1}, which is typical for a perfluorinated internal azaalkene.[9] The ^{19}F NMR spectrum of compound 4 contains six signals with intensity in the proportions $1:3:3:2:2:2$. At 22 °C the resonances at δ_F -26.66, -92.83 and -94.49 are broad. At -10 °C these signals sharpen into multiplets and the value of the coupling constant between the
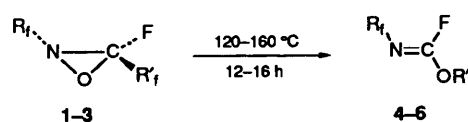
Compound	R_f	R'_f
1, 4	C_3F_7	C_2F_5
2, 5	C_4F_9	C_3F_7
3, 6	C_6F_{13}	C_5F_{11}

vinylic fluorine and the CF_2 group attached to nitrogen (18 Hz) indicates that compound 4 has the Z configuration. The temperature dependence of the NMR spectrum can be explained in terms of an inversion at nitrogen.[10]

Further evidence for the structure of the vinyl ethers comes from the reaction of compound 5 with CsF in acetonitrile, resulting in the formation of a mixture of perfluoropropionyl fluoride and azaalkene 7. A probable reaction is indicated in Scheme 1.

$$5 + CsF \longrightarrow [C_4F_9\overline{N}CF_2OC_3F_7]Cs^+ \longrightarrow$$
$$8$$

$$C_4F_9N=CF_2 + Cs^+(^-OCF_2CF_2CF_3) \xrightarrow{-i} C_3F_7C(F)=NCF_3 +$$
$$9 \qquad\qquad\qquad\qquad\qquad\qquad\qquad 7$$
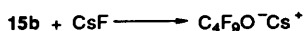$$C_2F_5C(O)F$$

Scheme 1 *Reagent:* i, CsF

Addition of CsF to compound 5 leads to the formation of the caesium salt of anion 8, which further eliminates the perfluoropropoxy anion to give the terminal azaalkene 9. Under the reaction conditions, the O-anion eliminates fluoride ion to give perfluoropropionyl fluoride and isomerization of imine 9 by F^- leads to the formation of compound 7.

Reactions with SbF_5.—In contrast to PFAPO, oxaziridines 1–3 are stable in the presence of the strong Lewis acid SbF_5 at 22 °C, but at 100 °C they rapidly rearrange into the alkoxy imines 10–12. Compounds 10–12 are colourless liquids which are stable to further reaction or decomposition at 100 °C. The IR spectra exhibit strong absorptions near 1700 cm^{-1} consistent with the imine. The ^{19}F NMR spectra are also in good agreement with the structure of the alkoxy imines, and on steric grounds the E configuration is assumed. The structures are also

Table 1 Reactions of $C_4F_9N\text{-}CO(F)C_3F_7$ **2** with carbonyl compounds

$$2 + (R_f)_2CO \xrightarrow{\text{CsF}} (R_f)_2CFON=CFC_3F_7 + C_3F_7C(O)F + C_4F_9ON=CFC_3F_7$$
$$\qquad\qquad\qquad\qquad\quad 17\text{-}20 \qquad\qquad\qquad 15b \qquad\qquad\qquad 11$$

Quantity 2[a]	Quantity $(R_f)_2CO$[a]	Quantity CsF[a]	Time (t/h) at 22 °C[b]	Products (%)[c]
2	$(CF_3)_2CO$, 4	0.9	2	17 (95), 15b
4	$CF_3(CF_2Cl)CO$, 8	1.2	4	18 (94), 15b
2	$(CF_2Cl)_2CO$, 3	1.5	12	19 (35), 11, 15b
4	F_2CO, 9	0.9	12	20 (40), 11, 15b, other[d]
2	$(i\text{-}C_3F_7)_2CO$, 2	1.3	1	11[d]

[a] mmol. [b] MeCN (4–6 cm^3). [c] Isolated yield. Isolated yield of compounds **11** and **15b** was not determined. Conversion of substrate **2** was 100% in each case. [d] See Experimental section.

Compound	R_f	R'_f
10	C_3F_7	C_2F_5
11	C_4F_9	C_3F_7
12	C_6F_{13}	C_5F_{11}

in agreement with other fluorinated oximes prepared by a different route involving dehydrohalogenation of alkoxy amines. $R_xON(H)CF_3$.[11-13]

The reaction with SbF_5 occurs at a temperature well below that required for the thermal rearrangement of ethers **1–3**. Therefore we assume that the two reaction types do not occur *via* the same initial ring-opening step.* This reaction may occur by a process involving abstraction of fluoride by SbF_5 from the CF_2 group attached to nitrogen, followed by the isomerization of the cyclic azacation **13** into a linear carbocation **14**. Addition of fluoride ion to this cation results in the formation of the final product (Scheme 2). The process by which cation **13** rearranges and the ring oxygen is inserted into the nitrogen–carbon bond is not obvious but this rearrangement bears some similarity to the previously observed rearrangements of species $R_f\text{-}N\text{-}NFCF_2$ ($R_f = CF_3$, SF_5) into $R_fN=NCF_3$[14] and the initial step of the reaction with SbF_5 is consistent with the reaction of cyclic perfluorinated tertiary amines with SbF_5.[15]

Scheme 2 *Reagent:* i, SbF_5

PFAPO reacts with SbF_5 to give a cyclic dimer[2] and hydrocarbon oxaziridines form nitrones on reaction with Lewis acids,[16] but no evidence for the formation of dimeric products or N-oxides has been found in these reactions.

Reactions with Nucleophiles.—Perfluoro-2,3-dialkyloxaziridines are much less sensitive to nucleophilic attack than is PFAPO or its analogues $\overline{OCF_2\text{-}NR_x}$[1c,4] which isomerize readily in the presence of KF or NaF at room temperature.

* A referee pointed out that it is impossible to distinguish which original perfluoroalkyl group (R_f or R'_f) is bound to oxygen, because R_f and R'_f always differ by one CF_2 group. Nevertheless we prefer the product as shown and future work will address this issue.

Compounds **5** and **6** react with dry CsF in the absence of solvent only at or above 100 °C. This results in the formtion of a 1:1 mixture of N-fluoro imine and acyl fluoride in a high yield.

This reaction may proceed according to the mechanism proposed for the reaction of PFAPO with metal fluorides, initiated by attack of fluoride ion on the positively polarized nitrogen atom of the oxaziridine ring.[1]

It has previously been shown that compounds of the type $R_fC(O)N(X)R'_f$ and $FC(O)N(X)R_x$ are unstable in the presence of active metal fluorides.[17] Thus the products $R_fN(F)C(O)R'_f$ analogous to $CF_3N(F)C(O)F$ formed from PFAPO and fluoride are not isolated. This difference can be rationalized on the basis of the relative stability and nucleophilicity of the anions R_fNF^- [equation (1)].

$$R_fNF^- \rightleftharpoons R'_fCF=NF + F^- \qquad (1)$$

In the case of $R_f = CF_3$, the equilibrium favours the anion and a mixtue of $CF_2=NF$ ($R'_f = F$) and $R_fC(O)F$ react in the presence of active metal fluorides to give $CF_3N(F)C(O)R_f$.[18] When $R_f = C_2F_5$ and higher in R_fNF^-, this equilibrium lies far in the direction of the imine and reactions of R_fNF^- in these cases can be observed only in polar solvents with high fluoride ion activity.[8]

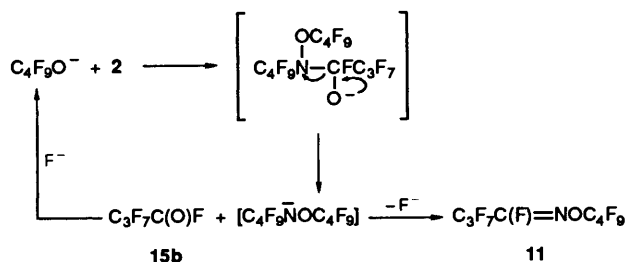Surprisingly, the reaction of compound **2** with CsF as a

catalyst in MeCN takes place readily at 22 °C and the alkoxy imine **11** is formed as the sole product of the reaction. We propose that the reaction in MeCN proceeds by a nucleophilic chain process (Scheme 3).

(*a*) *initiation:*

$$2 + CsF \longrightarrow 15a + 15b$$

$$15b + CsF \longrightarrow C_4F_9O^-Cs^+$$

(*b*) *propagation:*

Scheme 3

Only a trace of the acyl fluoride **15b** is observed in MeCN, in contrast to the reaction of compound **2** with CsF without solvent. This is reasonable based on the enhanced reactivity of $R_fC(O)F$ with fluoride ion in polar aprotic solvents.

The reactions of compound **2** with fluorinated carbonyl compounds in MeCN in the presence of CsF are in good agreement with the proposed reaction Scheme 3. Reaction of hexafluoro- and chloropentafluoro-acetone with the oxaziridine in the presence of catalytic amounts of CsF results in the formation of the acyl fluoride **15b** and the alkoxy imines **17** and **18**.
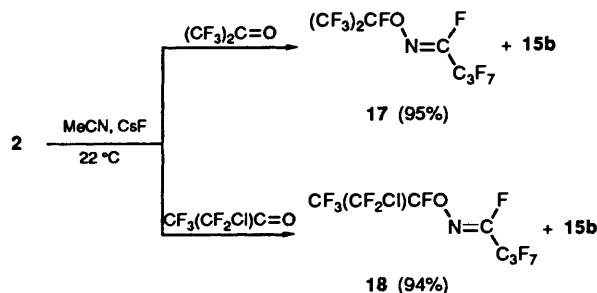
Reaction of 1,3-dichlorotetrafluoroacetone and difluorophosgene (carbonyl difluoride) with compound **2** in the presence of CsF as a catalyst leads to the formation of a mixture of the corresponding alkoxy imine, the acyl fluoride **15b** and oxime **11** (Table 1).
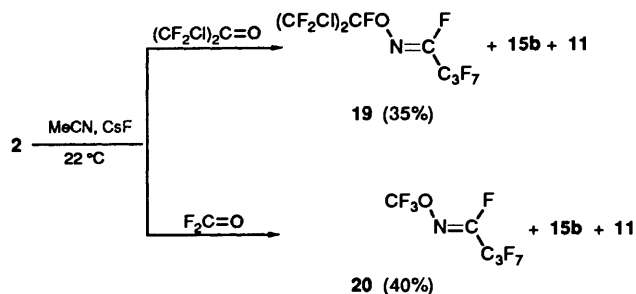
Imine **11** is a single product in the reaction of compound **2** with sterically hindered perfluorodiisopropyl ketone.

$$2 + [(CF_3)_2CF]_2C=O \xrightarrow[\text{MeCN, CsF}]{1 \text{ h, } 22 °C} 11 + [(CF_3)_2CF]_2C=O$$
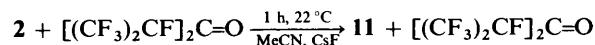
These results clearly indicate that as the reactivity of the carbonyl substrate with CsF decreases, reaction of the oxaziridine with fluoride ion becomes the dominant reaction. Similar results would be expected with oxaziridines **1** and **3** but this was not studied.

Again, in the case of PFAPO, reaction with CsF and COF_2 or $(CF_3)_2CO$ leads to the isolation of $CF_3N(OR_f)C(O)F$ and there is no formation of COF_2 by elimination of CF_3NOR_f. Similarly, several imines of the type $CF_2=NOR_x$ provide abundant evidence of the special trifluoromethyl effect in stabilizing anions of the type CF_3NOR_x.[13]

Conclusions.—Unusual new reactions of perfluoro-2,3-dialkyloxaziridines have been demonstrated. The unusual rearrangements of the oxaziridines leading to the insertion of the ring-oxygen atom into the R_f–N< (SbF_5) and >CF–R'_f (thermal) bonds are novel. These oxaziridines also undergo more typical reactions involving ring opening by nucleophiles but their reactivity is much lower than that of previously studied 2-perhalogenoalkyl-3,3-difluorooxaziridines.

Experimental

Reagents.—'Difluorophosgene' (carbonyl difluoride) and polyfluoro ketones were obtained from commercial sources. CsF was dried for 2 h with a Bunsen burner and a porcelain dish and was used directly after being dried. MeCN was distilled over P_2O_5 and stored over CaH_2. Oxaziridines 1–3 were prepared as described previously.[7] Compounds **15a,b** and **16a,b** were identified by comparison with authentic samples, and compound **7** was identified by comparison of ^{19}F NMR, IR and mass spectral data with the literature values.[20]

General Procedure for Thermal Isomerization of Oxaziridines.—The oxaziridine (2.8–5 mmol) was heated for 12–20 h at 150–170 °C in a 5 cm³ glass sample tube fitted with a Teflon–glass valve. The yields of product ethers **4–6** were quantitative.

Perfluoro-1-*ethoxy*-2-*azapent*-1-*ene* **4**. B.p. 76–77 °C; v_{max} (liq)/cm⁻¹ 1768s, 1346s, 1291s, 1243s, 1164s, 1102s, 1023s, 927m, 858m and 751s; m/z (CI, major) (intensity %) 350 [(M + 1)⁺, 13], 330 [(M + 1 − HF)⁺, 100], 230 [(M − C₂F₅)⁺, 15] and 214 [(M − C₂F₅O)⁺, 15]; δ_F ($CF_3^ACF_2^ECF_2^CN=CF^DOCF_2^E-CF_3^B$) (CDCl₃; 263 K) A −81.50 (3 F t), B −86.70 (3 F, t), C −92.34 (2 F, dm), D −25.92 (1 F, t quint.), E −94.31 (2 F, s)

and F -130.10 (2 F, d); $J_{\text{C-D}}$ 18, $J_{\text{A-C}}$ 8, $J_{\text{F-D}}$ 2, $J_{\text{B-E}}$ 1.5 and $J_{\text{D-E}}$ < 1.0 Hz.

Perfluoro-1-propoxy-2-azahex-1-ene **5**. B.p. 119–120 °C; ν_{max}(liq)/cm^{-1} 1771vs, 1343m, 1295s, 1235vs, 1094m, 1055m, 1008s, 987m, 964m, 912m, 882m, 847m and 749m; m/z (CI, major) 450 [(M + 1)$^+$, 66], 430 [(M − F)$^+$, 91], 280 [(M − C$_3$F$_7$)$^+$, 20], 264 [(M − C$_3$F$_7$O)$^+$, 10], 219 (C$_4$F$_9$$^+$, 9) and 169 (C$_3F_7$$^+$, 100); δ_F (CF$_3^ACF_2^CCF_2^ECF_2^C$N=CF^{D}OCF$_2^ECF_2^FCF_3^B$) (293 K) A, B -82.70 (6 F, q), C -91.97 (2 F, br s), D -26.30 (1 F, br s), E -90.28 (2 F, br s), F -126.81 (4 F, q) and G -130.05 (2 F, br s); $J_{\text{C-D}}$ 16 (decoupling experiment), $J_{\text{A-F}} = J_{\text{B-D}} = 10$, $J_{\text{C-G}}$ 11 and $J_{\text{D-F}}$ 5 Hz (Found: C, 20.95; F, 72.3; N, 4.0. C$_8$F$_{17}$NO requires C, 21.38; F, 71.93; N, 3.12%).

Perfluoro-1-pentoxy-2-azaoct-1-ene **6**. B.p. 194–195 °C; ν_{max}(liq)/cm^{-1} 1770vs, 1237vs, 1204vs, 1145s, 1089m, 1043m, 1022m, 985m, 926m, 876m, 805m, 745s, 709s, 652m and 525m; m/z (CI, major) 650 [(M + 1)$^+$, 14], 634 [(M + 1 − O)$^+$, 10], 630 [(M − F)$^+$, 9], 350 [(M + 1 − C$_6$F$_{12}$)$^+$, 100], 330 [(M − C$_6$F$_{13}$)$^+$, 78], 319 (C$_6$F$_{13}$$^+$, 7), 269 (C$_5F_{11}$$^+$, 22), 219 (C$_4F_9$$^+$, 10), 169 (C$_3F_7$$^+$, 22) and 119 (C$_2F_5$$^+$, 59); δ_F (CF$_3^A$[CF$_2^F$]$_4$-CF$_2^C$N=CF^{D}OCF$_2^E$[CF$_2^F$]$_3CF_3^B$) (293 K) A, B -81.26 (6 F, quint.), C -91.48 (2 F, br s), D -26.08 (1 F, m), E -88.93 (2 F, br s), F -122.58 (2 F, m), -123.45 (2 F, m), -125.63 (4 F m) and -126.70 (6 F, m); $J_{\text{A-F}} = J_{\text{B-F}} = 10$ Hz; other coupling constants not readily determined.

Reaction of Compound **5** *with* CsF.—Compound **5** (1.78 mmol) was allowed to react at 22 °C with dry CsF (0.67 mmol) in MeCN (1 cm^3). After 30 min, trap-to-trap distillation *in vacuo* (-70, -120, -196 °C) gave compound **7** (0.83 mmol, 93%) in the -120 °C trap and C$_2$F$_5$C(O)F (0.82 mmol, 92%) in the -196 °C trap.

Reaction of Oxaziridines **1–3** *with* SbF$_5$.—Oxaziridines **1–3** (2–3 mmol) and SbF$_5$ (1.4–1.8 mmol) were placed in a 5 cm^3 glass sample tube fitted with a Teflon–glass valve and the reaction mixture was kept at 100–110 °C for 2–4 h. The reaction mixture was then poured into ice-water and the lower layer was separated by pipette and dried with P$_2$O$_5$.

Perfluoro-4-oxa-5-azaoct-5-ene **10**. Yield 91%; b.p. 75–76 °C; ν_{max}(liq)/cm^{-1} 1700m, 1332s, 1234vs, 1199vs, 1181vs, 1137vs, 1027s, 1000s, 928m, 907m, 783m, 750m and 732s; m/z (CI, major) 350 [(M + 1)$^+$, 55], 334 [(M + 1 − O)$^+$, 3], 330 [(M − F)$^+$, 100], 230 (C$_4$F$_8$NO$^+$, 16.6) and 119 (C$_2$F$_5$$^+$, 15); δ_F(CF$_3^ACF_2^FCF_2^C$ON=CF^{D}CF$_2^ECF_3^B$) A -82.05 (3 F, t), B -83.60 (3 F, dt), C -89.90 (2 F, dtq), D -70.40 (1 F, tq), E -120.70 (2 F, dq) and F -129.21 (2 F, t); $J_{\text{A-C}}$ 7, $J_{\text{D-E}}$ 15, $J_{\text{B-D}}$ 4, $J_{\text{B-E}}$ 2.5, $J_{\text{C-F}}$ 3 and $J_{\text{C-D}}$ 1.5 Hz.

Perfluoro-5-oxa-6-azadec-6-ene **11**. Yield 85%; b.p. 116–117 °C; ν_{max} (liq.)/cm^{-1} 1705m, 1302m, 1251s, 1143s, 1063w, 989w, 928m, 899m and 735s; m/z (EI, major) 430 [(M − F)$^+$, 13], 330 [(M − C$_2$F$_5$)$^+$, 1], 280 [(M − C$_3$F$_7$)$^+$, 6], 219 (C$_4$F$_9$$^+$, 6), 169 (C$_3F_7$$^+$, 38), 131 (C$_3F_5$$^+$, 13), 119 (C$_2F_5$$^+$, 10) and 69 (CF$_3$$^+$, 100); δ_F (CF$_3^ACF_2^FCF_2^ECF_2^C$ON=CF^D-CF$_2^ICF_2^GCF_3^B$) A, B -81.10 and -81.65 (6 F, t), C -88.90 (2 F, t quint.), D -68.40 (1 F, m), E -125.52 (2 F, q), F -127.12 (2 F, quint.), G -127.22 (2 F, q) and I -118.54 (2 F, dq); $J_{\text{I-D}}$ 12, $J_{\text{B-I}}$ 8, $J_{\text{C-F}}$ 9, $J_{\text{A-E}}$ 8, $J_{\text{C-D}}$ 2 and $J_{\text{D-G}}$ 6 Hz (Found: C, 21.0; F, 72.3; N, 3.7. Calc. for C$_8$F$_{17}$NO: C, 21.38; F, 71.93; N, 3.12%).

Perfluoro-7-oxa-8-azatetradec-8-ene **12**. Yield 88%; b.p. 191–192 °C; ν_{max} (liq)/cm^{-1} 1698m, 1343m, 1323m, 1237vs, 1203s, 1144s, 1094m, 1066m, 985m, 924m, 847m, 813m, 743m, 730s, 710m, 659m and 525m; m/z (CI, major) 650 [(M + 1)$^+$, 100], 634 [(M + 1 − O)$^+$, 14], 630 [(M − F)$^+$, 63], 380 [(M − C$_5$F$_{11}$)$^+$, 56] and 319 (C$_6$F$_{13}$$^+$, 35); δ_F (CF$_3^ACF_2^F$-[CF$_2^G$]$_3CF_2^C$ON=CF^{D}CF$_2^E$[CF$_2^G$]$_3CF_3^B$) A, B -81.25 (6 F, m), C -88.55 (2 F, t), D -69.96 (1 F, m), E -117.60 (2 F, dt), F

-126.69 (4 F, m), G -122.83 (4 F, m), -123.43 (4 F, m) and -124.82 (2 F, m); $J_{\text{D-E}}$ 12, $J_{\text{E-G}}$ 12 and $J_{\text{C-G}}$ 9 Hz.

Reaction of Oxaziridines **2** *and* **3** *with* CsF.—In a 75 cm^3 stainless steel autoclave, dry CsF (20 mmol) and **2** (23 mmol) were kept at 100–110 °C for 12 h. Trap-to-trap distillation (-30, 196 °C) gave a 1:1 mixture of products **15a** and **15b** (35 mmol, 76%). Under the same conditions compound **3** (15.5 mmol) and CsF (20 mmol) produced a mixture of products **16a** and **16b** (ratio 1:1) (26 mmol, 84%).

Reaction of compound **2** *with* CsF *in* MeCN.—Compound **2** (1.33 mmol) was added in one portion to a stirred suspension of CsF (1.32 mmol) in MeCN (3 cm^3) at 22 °C. After 2 h the reaction mixture was diluted with 10% hydrochloric acid (10 cm^3) and the bottom layer was removed by pipette and dried over P$_2$O$_5$. Compound **11** (0.52 g, 87%) was isolated as the only fluorinated product.

Reaction of compound **2** *with Carbonyl Compounds.*—The oxaziridine **2** (2–4 mmol) was allowed to react with an excess of the carbonyl compound in the presence of dry CsF (0.9–1.5 mmol) in MeCN for 1–12 h (Table 1). The reactions were monitored by NMR spectroscopy and the product ratios were determined by integration as: (hexafluoroacetone): **17** and **15b** (1:1); (chloropentafluoroacetone): **18** and **15b** (1:1); (1,3-dichlorotetrafluoroacetone): 48% **19**, 45% **11**, 7% **15b**; (difluorophosgene): 51% **20**, 13% **11**, 13% **15b**, 23% other unidentified products; (Perfluorodiisopropyl ketone): starting ketone and **11** (1:1). Compounds **17** and **18** were isolated as described above in 94 and 95% yield. Compound **19** was isolated by distillation on a small spinning-band column in 35% yield, and compound **20** (40%) by preparative GLC (Halocarbon K-352, 3 m; He, 20 cm^3 min^{-1}; oven temperature 30 °C).

Perfluoro-2-methyl-3-oxa-4-azaoct-4-ene **17**. B.p. 95–96 °C; ν_{max}(liq)/cm^{-1} 1767w, 1703m, 1382m, 1240s, 1143m, 1115s, 1025m, 987w, 918w, 854w, 748m and 734m; m/z (CI, major) 400 [(M + 1)$^+$, 74], 383 [(M − O)$^+$, 6], 380 [(M − F)$^+$, 100], 230 [(M − C$_3$F$_7$)$^+$, 20], 214 [(M − C$_3$F$_7$O)$^+$, 10) and 169 (C$_3$F$_7$$^+$, 57); δ_F [(CF$_3^A$)$_2$CF^{F}ON=CF^{D}CF$_2^CCF_2^ECF_3^B$] A -77.76 (6 F, d), B -80.95 (3 F, t), C -118.45 (2 F, m), D -68.95 (1 F, m), E -127.20 (2 F, d) and F -138.60 (1 F, oct.); $J_{\text{C-D}}$ 14, $J_{\text{B-C}}$ 9, $J_{\text{D-E}}$ 5, $J_{\text{A-F}} = J_{\text{D-F}} = 2$ Hz.

1-Chloro-1,1,2,5,6,6,7,7,8,8,8-undecafluoro-2-trifluoromethyl-3-oxa-4-azaoct-4-ene **18**. B.p. 116–117 °C; ν_{max}(liq)/cm^{-1} 1771w, 1703m, 1327m, 1227vs, 1142s, 1113s, 1056m, 950m, 849m and 745m; m/z (CI, major) 418 and 416 [(M + 1)$^+$, 17, 70], 398 and 396 [(M − F)$^+$, 18, 100], 380 [(M − Cl)$^+$, 35], 330 [(M − CF$_2$Cl)$^+$, 19] and 169 (C$_3$F$_7$$^+$, 63); δ_F [CF$_3^A$(CF^{G}F$^{G'}$Cl)CF^{F}ON=CF^{D}CF$_2^CCF_2^ECF_3^B$] A -75.42 (3 F, t), B -81.06 (3 F, t), C -118.50 (2 F, dpent. d), D -69.42 (1 F, tt), E -127.32 (2 F, d), F -134.30 (1 F, d), G -65.10 (1 F, dq) and G' -67.40 (1 F, dpent. d) typical A:B pattern; $J_{\text{G-G'}}$ 183, $J_{\text{F-G}} = J_{\text{A-G}} = 11$, $J_{\text{B-C}}$ 9, $J_{\text{A-G'}}$ 10, $J_{\text{C-D}}$ 14, $J_{\text{E-D}}$ 4, $J_{\text{D-F}}$ 1.5 and $J_{\text{F-G'}}$ 3.

1-Chloro-2-(chlorodifluoromethyl)-1,1,2,5,6,6,7,7,8,8,8-undecafluoro-3-oxa-4-azaoct-4-ene **19**. B.p. 154–155 °C; ν_{max}(liq)/cm^{-1} 1701m, 1371m, 1350m, 1238s, 1141s, 1109s, 933m, 820m and 740m; m/z (CI, major) 436, 434 and 432 [(M + 1)$^+$, 5, 18, 33], 416, 414 and 412 [(M − F)$^+$, 9, 27, 52], 398 and 396 [(M − Cl)$^+$, 13, 63], 348 and 346 [(M − CF$_2$Cl)$^+$, 8, 21] and 169 (C$_3$F$_7$$^+$, 100); δ_F [CF^{A}F^{B}Cl(CF$^{A'}$CF$^{B'}$Cl)CFON=CF^{E}CF$_2^C$-CF$_2^G$CF$_3^C$] A, A' -62.55 (2 F, m), B,B' -64.00 (2 F, m, typical AB spin system), C -81.30 (3 F, t), D -118.60 (2 F, m), E -70.57 (1 F, tt), F -129.78 (1 F, tq) and G -127.44 (2 F, d); $J_{\text{A-B}}$ 183, $J_{\text{C-D}}$ 8, $J_{\text{F-D}}$ 13, $J_{\text{F-G}}$ 5, $J_{\text{D-E}}$ 13, $J_{\text{D-G}}$ 6 and $J_{\text{E-F}}$ < 2 Hz.

Perfluoro-2-oxa-3-azahept-3-ene **20**. B.p. 16 °C; ν_{max}(gas)/cm^{-1} 1705m, 1330m, 1292vs, 1202vs, 1148m, 1122m, 1088w,

1022m, 958–938m, 910w, 814w and 750m; m/z (CI, major) 300 [$(M + 1)^+$, 88], 280 [$(M - F)^+$, 100], 230 [$(M - CF_3)^+$, 1], 214 [$(M - CF_3O)^+$, 6] and 180 [$(M - C_2F_5)^+$, 31]; δ_F ($CF_3^A ON{=}CF^D CF_2^C CF_2^E CF_3^B$) A -65.80 (3 F, d), B -80.98 (3 F, t), C -118.63 (2 F, m), D -69.68 (1 F, sept.) and E -126.95 (2 F, d); J_{D-E} 6, J_{C-D} 13, J_{C-B} 9, J_{A-D} 2 Hz.

Acknowledgements

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